Extension of Dunham's Analytic Treatment of Highly Resolved Infrared and Microwave Spectra of Diatomic Molecules

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We extended Dunham's approach to analytic treatment of vibration−rotational spectra of diatomic molecules and applied the method to GaH and LiH in their ground electronic states $X^1\Sigma^+$. Published wavenumbers of assigned transitions are reproduced with fewer parameters for potential energy than reported elsewhere. From parameters $t_0^{\text{Ga,H}}$ representing nonadiabatic rotational effects, we estimate at R_0 the rotational g factor for $^{69}\text{Ga}^1\text{H}$ $g_0 = -3.493(61)$ and electric dipolar moment $\mu_0 = 6.9(44) \times 10^{-30}$ Cm for assumed polarity $^+\text{GaH}^-$. The former conforms acceptably with $g_0 = 3.4440$ calculated with the second order polarization propagator approximation.

1 Introduction

The standard procedure to reduce infrared (IR) and microwave (MW) spectra of diatomic molecules to parameters of a potential-energy function is based on an analytic approach developed by Dunham[1] in 1932.

To determine states of quantized energy of vibration−rotational diatomic systems, Dunham[1] solved Schrödinger's equation

$$\left[-B_0 \frac{d^2}{dx^2} + \frac{B_0 J(J+1)}{(1+x)^2} + V(x) - E_{vJ}^{BO}\right]\psi_{vJ}(x) = 0 \quad (1)$$

including the Born−Oppenheimer (BO) internuclear potential energy

$$V(x) = a_0 x^2 \left(1 + \sum_{i=1} a_i x^i\right) \qquad x = (R - R_0)/R_0 \quad (2)$$

by making use of a semiclassical (Brillouin−Kramers−Wentzel) method to produce eigenvalues in a form

$$E_{vJ}^{BO} = \sum_{k,l=0} Y_{kl}(R_0, a_i)(v + 1/2)^k [J(J+1)]^l \quad (3)$$

In eqs 1−3, $B_0 = \hbar^2/(2mR_0^2)$ denotes[2] the equilibrium rotational parameter and m the reduced mass of the system, R is the instantaneous intermuclear separation, and R_0 its value at equilibrium, according to conventional notation; Y_{kl} are Dunham's term coefficients[1] that depend on parameters R_0 and a_i, whereas J and v are rotational and vibrational quantum numbers, respectively.

Thus, by fitting measured vibration−rotational spectra to terms E_{vJ}^{BO} one can readily, either directly or indirectly (through intermediate quantities Y_{kl}), evaluate paramters R_0 and a_i that well define a potential-energy function (2) within a range $R \in \langle 0, 2R_0 \rangle$ of internuclear separation.[3]

With increased precision and resolution of spectral measurements, it became clear that this approach works satisfactorily

for only poorly resolved bands. For highly resolved spectra, particularly those obtained with Fourier transform spectrometers and diode lasers, serious discrepancy between theory and experiment is reported.[4−11] In adapting of Dunham's method to contemporarily measured precise spectral data, several improvements are proposed; they include introduction of representation other than that in eq 2 for internuclear potential energy,[12−15] adiabatic and nonadiabatic rotational (vibrational) corrections[16−19] to BO eigenenergies eq 3, and application of other methods[20−23] to solve Schrödinger's equation (1).

Ogilvie applied[24] an expansion for potential energy[15]

$$V(x) = c_0 z^2 (1 + \sum_{i=1} c_i z^i) \qquad z = 2(R - R_0)/(R + R_0) \quad (4)$$

and an hypervirial perturbative approach[21] to solve Schrödinger's equation[19]

$$\left(-B_0 \frac{d^2}{dx^2} + U_{vJ}(x) - E_{vJ}\right)\psi_{vJ}(x) = 0 \quad (5)$$

$$U_{vJ}(x) = \frac{B_0 J(J+1)[1 + \alpha(x) - \beta(x)]}{(1+x)^2} + V(x)[1 - \beta(x)] + V'(x) + E_{vJ}^{BO}\beta(x) \quad (6)$$

with adiabatic $V'(x)$ and nonadiabatic rotational $\alpha(x)$ and vibrational $\beta(x)$ corrections to BO energies E_{vJ}^{BO}.

The adiabatic term reflects the dependence of internuclear potential energy on not only the distance between nuclei but also their relative momenta; nonadiabatic rotational effects reflect the fact that electrons fail to follow perfectly the nuclei rotating about the center of molecular mass, whereas nonadiabatic vibrational effects appear because of vibrational inertia of electrons.

All radial functions in eq 6 were expanded into a series of variable z that remains finite $-2 \leq z < 2$ throughout the range of molecular existence $0 \leq R < \infty$. Hence the potential expansion (eq 4) converges in the range $R \in \langle R_0/3, 3R_0 \rangle$, significantly extended relative to the convergence radius of coordinate x.

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According to Ogilvie's notation,[19,24] the functions representing adiabatic and nonadiabatic effects take the forms

$$V'(x) = m_e \sum_{i=1} \sum_{\mu=a,b} u_i^\mu m_\mu^{-1} z^i \qquad (7)$$

$$\alpha(x) = m_e \sum_{i=0} \sum_{\mu=a,b} t_i^\mu m_\mu^{-1} z^i \qquad (8)$$

$$\beta(x) = m_e \sum_{i=0} \sum_{\mu=a,b} s_i^\mu m_\mu^{-1} z^i \qquad (9)$$

Here m_e, m_a, and m_b are masses of electron and nuclei.

The hypervirial perturbative approach provides eigenenergies[24]

$$E_{vJ} = \sum_{k,l=0} \sum_{\mu=a,b} (Y_{kl} + Z_{kl}^{r,\mu} + Z_{kl}^{v,\mu})(v+1/2)^k[J(J+1)]^l \quad (10)$$

in which $Z_{kl}^{r,a(b)}$ and $Z_{kl}^{v,a(b)}$ are adiabatic and rotational (vibrational) nonadiabatic terms depending on radial parameters $u_i^{a,b}$, $t_i^{a,b}$, and $s_i^{a,b}$.

The energy formula (eq 10) is implemented in a computer program Radiatom.[24] Its application in spectral analysis provided satisfactory reproduction of observed vibration−rotational transitions of diatomic species and valuable information on their electric and magnetic properties.[25−30] The latter are represented by the dipolar moment $\mu(x)$ and rotational g factor $g_J(x)$ (that can be evaluated from Stark and Zeeman experiments, respectively) simply related[30] to nonadiabatic parameters $t_i^{a(b)}$

$$\mu(x) = (eR/2) \sum_{i=0} (t_i^a - t_i^b) z^i \qquad (11)$$

$$g_J(x) = m_p \sum_{i=0} \sum_{\mu=a,b} t_i^\mu m_\mu^{-1} z^i \qquad (12)$$

Here e and m_p denote elementary charge and protonic mass, respectively; electric polarity of the molecule is assumed to be $^+AB^-$.

Another algorithm for reduction of infrared and microwave spectra, based on a so-called deformationally self-consistent (DS-c) procedure[31] (DS-cP), is reported; its application to highly resolved spectra of GaH[32], LiH[33], and GeS[34] provided satisfactory reproduction of experimental data and invoked fewer fitted parameters than in Ogilvie's approach.[26,29,30] A computing program DS-cP employs analytic expressions for a purely vibrational contribution to molecular eigenenergies, but the equilibrium reference conformation in a given state is calculated numerically using bisection[31] or the Newton−Raphson algorithm.[36] Such an approach inherently lacks explicit analytic expressions and requires major modification of programs used in spectral analysis so far.

The main objective of this work is to present a further method to investigate highly resolved spectra of diatomic molecules; this method incorporates all advantages of the DS-c approach but is formulated in purely analytical terms. All mathematical formulae involved in this algorithm are derived with a symbolic computation (Maple) processor, following which we apply standard software used in spectral analysis.

2 Method

A standard procedure to solve wave equation 5 consists of expansion of the effective potential (eq 6) into a series in a variable x and then applying a semiclassical[1] or hypervirial perturbative method[21] to produce eigenvalues (eq 10). This approach is well justified[32] for purely vibrational systems described by the BO potential (eq 2). For molecules endowed with a potential (eq 6), vibrational displacements of nuclei take place in a vicinity of a modified equilibrium conformation R_{vJ} defined according to the criterion for a minimum

$$\left[\frac{dU_{vJ}(x)}{dx}\right]_{x=x_{vJ}} = 0 \qquad x_{vJ} = (R_{vJ} - R_0)/R_0 \quad (13)$$

An alteration $R_0 \rightarrow R_{vJ}$ is a result of centrifugal deformation[31,32] and nonadiabatic vibrational effects of high order ($s_{i>0}^{a(b)}$) responsible for the appearance of the term $E_{vJ}^{BO}\beta(x)$ in the effective potential energy (eq 6) and additional v-dependence of R_{vJ}.

Starting from this basic idea, we express all terms in eq 5 with a modified variable dependent on (v, J)

$$\eta = (R - R_{vJ})/R_{vJ} \qquad (14)$$

to which, we apply a linear transformation

$$x = x_{vJ} + \eta(1 + x_{vJ}) \qquad (15)$$

Accordingly, we obtain a wave equation

$$\left[-B_{vJ}\frac{d^2}{d\eta^2} + U_{vJ}(\eta) - E_{vJ}\right]\psi_{vJ}(\eta) = 0 \qquad (16)$$

in which

$$B_{vJ} = \hbar^2/[2m(R_{vJ})^2] \qquad (17)$$

is an effective rotational parameter, whereas

$$U_{vJ}(\eta) = \frac{B_{vJ}J(J+1)[1 + \alpha(\eta) - \beta(\eta)]}{(1+\eta)^2} + V(\eta)[1 - \beta(\eta)]$$
$$+ V'(\eta) + E_{vJ}^{BO}\beta(\eta) \quad (18)$$

is an effective potential.

Expanding eq 18 into a Taylor series of variable η

$$U_{vJ}(\eta) = \sum_{n=0} b_n^{vJ}\eta^n \qquad (19)$$

$$b_n^{vJ} = (n!)^{-1}[d^n U_{vj}(\eta)/d\eta^n]_{n=0} \qquad (20)$$

we arrive at Schrödinger's equation

$$\left[-B_{vJ}\frac{d^2}{d\eta^2} + \sum_{n=0} b_n^{vJ}\eta^n - E_{vJ}\right]\psi_{vJ}(\eta) = 0 \qquad (21)$$

and a quantum mechanical force (in Heisenberg's representation)

$$\hat{F} = (i\hbar)^{-1}[\hat{p}, \hat{H}] = -\frac{dU_{vJ}(\eta)}{d\eta} \qquad (22)$$

in which $\hat{H}$ is a hamiltonian operator appearing in eq 21.

A state of dynamic equilibrium between deforming and restoring potential forces is achieved when

$$\hat{F} = 0 \Rightarrow \left[\frac{dU_{vJ}(\eta)}{d\eta}\right]_{\eta=0} = b_1^{vJ} = 0 \qquad (23)$$

We consequently exclude a linear term $b_1^{vJ}\eta$ from eqs 19 and

Infrared and Microwave Spectra of Diatomic Molecules

J. Phys. Chem. A, Vol. 103, No. 27, 1999 **5271**

21, arriving at an effective Schrödinger equation

$$\left[-B_{vJ}\frac{d^2}{d\eta^2} + a_0^{vJ}\eta^2\left(1 + \sum_{s=1} a_s^{vJ}\eta^s\right) - (E_{vJ} - b_0^{vJ})\right]\psi_{vJ}(\eta) = 0 \quad (24)$$

in which

$$a_0^{vJ} = b_2^{vJ} \qquad a_{s>0}^{vJ} = b_{s+2}^{vJ}/a_0^{vJ} \quad (25)$$

Equation 24 is amenable to direct solution in a semiclassical[1] or hypervirial perturbative[21] scheme; either produces eigenvalues in a form

$$E_{vJ} = b_0^{vJ} + \sum_{k=0} Y_{k0}(v + 1/2)^k \quad (26)$$

in which

$$b_0^{vJ} = U_{vJ}(\eta = 0) \quad (27)$$

and Y_{k0} are Dunham's vibrational coefficients Y_{k0}, in analytic expressions,[1] into which we substitute $\{R_0, a_s\} \rightarrow \{R_{vJ}, a_s^{vJ}\}$.

Expansion of potential energy (eq 18) in the effective variable η affects its convergence in comparison with (eq 18) expanded in the variable x. The latter procedure is applied so far as a point of departure for the semiclassical[1] and hypervirial perturbative determination[21] of eigenenergies (eqs 3 and 10). One can readily verify that η has a convergence radius $\mathcal{R} = 2R_{vJ}$, increasing with J because of centrifugal deformation. Formulation of molecular dynamics in terms of a dynamic reference conformation R_{vJ} instead of a static R_0 one hence implies that $\eta = (R - R_{vJ})/R_{vJ}$ describes purely vibrational displacements of nuclei about R_{vJ}, in contradistinction to $x = (R - R_0)/R_0$ describing vibrational deformational displacements of nuclei in a vicinity of R_0. In the latter case, the turning points for vibrational motion might escape from a domain of convergence ($R \geq 2R_0$) producing a divergent series and poor reproduction of the measured transitions.

3 Calculation of R_{vJ}

Eigenvalues (eq 26) contain unknown parameters x_{vJ} defined according to condition (eq 13) for equilibrium. In previous work,[31-36] we calculated the roots x_{vJ} of equation 13 numerically, with a bisection[31] or Newton–Raphson algorithm,[36] allowing us to fit spectral data in an iterative DS-c scheme.

Here, we derive x_{vJ} analytically using Maple according to a procedure described below. In the first step one differentiates an effective potential (eq 6)

$$f(x) = dU_{vJ}(x)/dx = -\hat{F} \quad (28)$$

Then eq 28 is expanded into a Taylor series in a variable x

$$f(x) = \sum_{i=0} h_i x^i \quad (29)$$

in which

$$h_i = (i!)^{-1}\left[\frac{d^i f(x)}{dx^i}\right]_{x=0} \quad (30)$$

This series is reverted to obtain

$$x(f) = \sum_{i=0} h_i^{-1} f^i \quad (31)$$

Putting $f = 0$ (equilibrium condition equivalent to $\hat{F} = 0$) one generates an analytic expression for x_{vJ}

$$x(f = 0) = h_0^{-1} = x_{vJ} \quad (32)$$

In calculations, we used a numerical formula for x_{vJ}, given as output from Maple in optimized Fortran code.

Having calculated x_{vJ}, one readily evaluates the dynamic reference conformation

$$R_{vJ} = R_0(1 + x_{vJ}) \quad (33)$$

whereas on substituting eq 32 into eq 26, the latter becomes a purely analytic formula describing energy states of a diatomic system.

4 Evaluation of function $\beta(x)$

Attempts to evaluate from spectra parameters $s_{i>0}^{a(b)}$, to represent nonadiabatic vibrational effects beyond zero order, were successful for only GaH[30] and LiH.[25,30] In the latter case all parameters $t_i^{Li,H}$, to represent nonadiabatic rotational effects, were constrained during the fit to values consistent with the rotational g factor and dipole moment of LiH (both from the quantum mechanical calculations[25,30] via eqs 11 and 12. As parameters $s_i^{a(b)}$ appear in eq 6 in the presence of E_{vJ}^{BO}, the latter contributes to eigenenergies (eqs 10 and 26).

In the standard approach,[24] E_{vJ}^{BO} is applied as the analytic formula (eq 3), consequently eq 10 takes an exact analytic form depending on parameters of the effective potential (eq 6). An alternative practical form of eq 6 reads

$$U_{vJ}(x) = \frac{B_0 J(J + 1)[1 + \alpha(x) - \beta(x)]}{(1 + x)^2} + V(x)[1 - \beta(x)] + V'(x) + E_{vJ}\beta(x) \quad (34)$$

whereas a replacement

$$E_{vJ} \rightarrow E_{vJ}^{BO} \quad (35)$$

transforming eq 34 into eq 6 is an arbitrary approximation.[16] To avoid it, we propose an approach in which E_{vJ} circulate during fitting of the spectral data, in numerical form.

For initial values of $E_{vJ} = 0$ (put automatically into eq 34), parameters for potential energy are fitted to experimental data using eigenenergies (eq 26) and a weighted nonlinear least-square routine with weights taken as inverse squares of uncertainties of experimental data. Because the term $E_{vJ}\beta(x)$ has a multiplicative form, it makes no contribution to energies (eq 26) calculated in the first step of the fitting procedure.

Evaluated parameters allow us to calculate numerical values of eigenenergies E_{vJ} from eq 26, which in the next step are reintroduced into eq 34. This iterative procedure is continued to obtain the best fit according to the following criteria: the minimum number of fitted parameters N consistent with the minimum value of normalized standard deviation $\hat{\sigma} \approx 1$, the maximum value of F-statistic, and the optimal values of estimated standard error σ_i of each fitted parameter i and of correlation coefficients $cc(i,j)$ between parameters i and j.

Although E_{vJ} are given in numerical form, they are more accurate than the BO energies employed in an approach with approximation (eq 35).

TABLE 1: Radial Parameters of GaH X$^1\Sigma^+$

	radiatom[a]	DS-cP[b]	EDA[c]
c_0/cm^{-1}	104630.43(22)	104630.59(25)	104631.26(28)
c_1	−1.347508(13)	−1.3474973(46)	−1.3474712(43)
c_2	1.038587(55)	1.038693(28)	1.038594(15)
c_3	−0.52229(17)	−0.52330(13)	−0.525419(69)
c_4	0.04522(59)	0.04441(31)	0.05397(36)
c_5	−0.1181(26)	−0.0919(18)	−0.615(11)
c_6	0.2556(72)	0.1834(46)	−0.0413(46)
c_7	−0.045(32)	−0.1811(34)	0.1596(91)
c_8	−1.63(11)		
t_0^{Ga}	−3.74(34)	−3.70(29)	−2.93(33)
t_1^{Ga}	4.57(70)		
t_0^{H}	−3.17043(62)	−4.20266(41)	−3.452(61)
t_1^{H}	7.366(19)	8.3165(51)	6.376(54)
t_2^{H}	−15.07(26)	−10.812(35)	−12.368(69)
t_3^{H}	16.22(42)	9.65(14)	12.86(13)
t_4^{H}		−11.93(46)	
s_0^{Ga}	0.539(81)		
s_1^{Ga}	14.2(38)		
s_0^{H}			−1.31(12)
u_1^{H}/10^4 cm^{-1}	−10.8091(10)		−7.96(64)
u_2^{H}/10^4 cm^{-1}		−32.5900(35)	5.02(69)
u_3^{H}/10^4 cm^{-1}	30.59(90)	59.741(83)	
u_4^{H}/10^4 cm^{-1}	−70.3(39)	−37.23(20)	
u_5^{H}/10^4 cm^{-1}	139(11)		
u_6^{H}/10^4 cm^{-1}	−250(28)		
R_0/10^{10} m	1.6601502(27)	1.6601491(20)	1.6601535(22)
$\hat{\sigma}$	0.920	1.087	0.957
F/10^{15}	3.30	10.17	11.78
N	23	18	18

[a] Data.[30] [b] Data.[32] [c] Parameter c_8 is constrained during the fit, according to eq 43.

This procedure is proposed to be suitable for evaluation of nonadiabatic vibrational function $\beta(x)$ including parameters $s_i^{a(b)}$. If the latter reduce to leading parametes $s_0^{a(b)}$, they are derivable directly from eq 26 given in a simplified form

$$E_{vJ} = (c_0^{vJ} + \sum_{k=0} Y_{k0}(v + 1/2)^k)/[1 - \beta(\eta = 0)] \quad (36)$$

in which

$$c_0^{vJ} = [B_{vJ}J(J+1)[1 + \alpha(\eta) - \beta(\eta)] + V(\eta)[1 - \beta(\eta)] + V'(\eta)]_{\eta=0} \quad (37)$$

and

$$\beta(\eta = 0) = m_e (s_0^a/m_a + s_0^b/m_b) \quad (38)$$

5 Application

To demonstrate advantages of this extended approach, we apply eigenvalues (eq 36) in a test analysis of spectral data of GaH, already intensively studied;[5,9,26,32,37] its highly resolved spectra provide an excellent means to test the BO approximation and to assess the extent of its deficiency for gallium and hydride (deuteride) centers.[5] Moreover, comparing the results obtained by particular authors, we can examine the status of existing theoretical models applied in contemporary spectral analyses.

As input data, we used 1094 transitions of ^{69}Ga^{1}H, ^{71}Ga^{1}H, ^{69}Ga^{2}H, and ^{71}Ga^{2}H, including 1045 lines from ref 37 and 49 unduplicated lines from ref 5 with $\Delta v = 1$ up to $v = 7$ and $J = 48$.

TABLE 2: Electric and Magnetic Properties of ^{69}Ga^{1}H X$^1\Sigma^+$ at Assumed Polarity $^+$GaH$^-$

	t_0^{Ga}	t_0^{H}	g_0	μ_0/10^{-30} Cm
radiatom[a]	−3.74(34)	−3.17043(62)	−3.223(11)	−7.3(47)
DS-cP[b]	−3.70(29)	−4.20266(41)	−4.2535(46)	6.6(38)
EDA	−2.93(33)	−3.452(61)	−3.493(61)	6.9(44)
EC[c]			⟨−2.9418, −3.4440⟩	⟨−0.2374, 1.5334⟩

[a] Data.[30] [b] Data.[32] [c] Data from electronic calculations.[40,41]

To ensure maximal significance of all fitted parameters of GaH, we constrained one potential-energy parameter c_8 in eq 4 to conform to the relation[38]

$$\mathcal{D}_e = \lim V(R)_{R\to\infty} = 4c_0(1 + \sum_{i=1} 2^i c_i) \quad (39)$$

and the known[39] thermochemical dissociation energy $\mathcal{D}_e = 22906$ cm^{-1} (2.84 eV) of ^{69}Ga^{1}H.

From nonadiabatic rotational parameters t_0^{Ga} and t_0^{H}, we estimate the permanent rotational g factor g_0 at R_0 and the electric dipolar moment μ_0 for ^{69}Ga^{1}H, using the leading parameters in eqs 11 and 12

$$\mu_0 = (eR_0/2)(t_0^{Ga} - t_0^{H}) \quad (40)$$

$$g_0 = m_p(t_0^{Ga}/m_{Ga} + t_0^{H}/m_H) \quad (41)$$

We compare the results with those produced with Radiatom and with Ds-cP and electronic calculations[40−43] in Table 2.

The proposed iterative procedure to evaluate nonadiabatic vibrational parameters $s_{i>0}^{a(b)}$ is applied to LiH. As input data, we used 543 pure rotational and vibration−rotational transitions of ^{7}Li^{1}H, ^{6}Li^{1}H, ^{7}Li^{2}H, and ^{6}Li^{2}H, including ten rotational lines,[44] 151 rotational and 377 vibration−rotational lines,[11] and 5 unduplicated vibration−rotational lines[45] with $\Delta v = 0$, 1 up to $v = 4$ and $J = 30$.

During the fit 14 parameters $t_{i=0−6}^{Li,H}$ were constrained to values specified in the work;[30] all other parameters were constrained to zero. The parameters $t_{i=0−6}^{Li,H}$ are derivable from the rotational g factor and dipolar moment of LiH, both from quantum mechanical computations,[25,30] and with the relationships reciprocal to eqs 11 and 12.

To compare potential-energy parameters of GaH and LiH generated with the Radiatom and with the present approach (EDA signifying an extended Dunham's approach), we expand all radial functions (eqs 4, 7−9 in variable z. The results of calculations are reported in Tables 1 and 3; they contain also parameters produced with the Radiatom with eigenenergies (eq 10) and DS-cP with R_{vJ} computed numerically. The uncertainty in parentheses is one estimated standard deviation in units of the last quoted digit of values of fitted parameters.

In the calculations, we used the vibrational term coefficients[1]

$$Y_{k0} = \sum_{h=0} Y_{k0}^{2h} \quad (42)$$

up to tenth order for GaH and sixth order for LiH. Consequently, expansion coefficients b_n^{vJ} of the effective potential energy (eq 6) contain derivatives up to twelfth order (GaH) and eighth order (LiH), respectively. Both Y_{k0} and b_n^{vJ} were calculated with symbolic processor Maple.

6 Discussion

The application of the extended approach enables reduction of wavenumbers of 1094 vibration−rotational transitions of GaH

Infrared and Microwave Spectra of Diatomic Molecules

J. Phys. Chem. A, Vol. 103, No. 27, 1999 **5273**

TABLE 3: Radial Parameters[a] of LiH X¹Σ⁺

	radiatom[b]	DS-cP[c]	EDA
c_0 cm⁻¹	65724.857(72)	65723.17(10)	65723.487(93)
c_1	−0.897208(12)	−0.897091(15)	−0.897117(10)
c_2	0.347847(76)	0.348249(30)	0.348153(21)
c_3	−0.086373(42)	−0.08863(38)	−0.08796(17)
c_4	−0.04529(18)	−0.04611(72)	−0.04653(37)
c_5	−0.0307(52)		
c_6	0.0921(96)		
$u_1^{Li}/10^4$ cm⁻¹	−5.740(44)	−5.704(45)	−5.671(43)
$u_1^{H}/10^4$ cm⁻¹	−5.2787(31)	−5.2706(44)	−5.2765(39)
$u_2^{H}/10^4$ cm⁻¹	7.245(70)	6.452(55)	5.989(70)
$u_3^{H}/10^4$ cm⁻¹	−7.53(14)	−7.02(19)	−1.53(26)
$u_4^{H}/10^4$ cm⁻¹		9.55(58)	
$s_0^{Li}/10^4$ cm⁻¹	−0.194(11)	2.064(14)	2.049(21)
s_0^{H}	−0.567(10)	−0.4359(86)	−0.374(10)
s_1^{H}			−2.00(16)
s_2^{H}	−0.591(112)	−2.99(17)	
$R_0/10^{10}$ m	1.594912(14)	1.59491217(51)	1.59491228(48)
$\hat{\sigma}$	1.095	1.090	1.077
$F/10^{15}$	5.0	5.98	6.56
N	15	14	13

[a] All parameters $t_{i=0-6}^{Li}$ and $t_{i=0-6}^{H}$ are constrained to values specified in the work.[30] [b] Data.[30] [c] Data.[36]

to $N = 18$ radial parameters rather than $N = 23$ in preceding work.[26,30] Despite the absence of these five superfluous parameters, the remaining ones satisfactorily reproduce data of GaH within uncertainties of spectral measurements.

From nonadiabatic rotational parameters t_0^{Ga} and t_0^{H}, we estimated the permanent rotational g factor $g_0 = -3.493(61)$ at R_0 and electric dipolar moment $\mu_0 = 6.9(44) \times 10^{-30}$ Cm for ^{69}Ga^{1}H. The first value conforms acceptably with $g_0 = -3.4440$ calculated with a second order polarization propagator approximation.[41] In contrast, the estimated magnitude of electric dipolar moment much exceeds results of several calculations: [41−43] $\langle -0.2374, 1.3489 \rangle \times 10^{-30}$ Cm, 1.5334×10^{-30} Cm, and 1.20×10^{-30} Cm, all at assumed polarity $^+$GaH$^-$. For comparison, values from Radiatom are $\mu_0 = -7.3(47) \times 10^{-30}$ Cm and $g_0 = -3.223(11)$; the latter is near the value $g_0 = -3.2452$ calculated with a coupled perturbed Hartree−Fock method.[41] Ds-cP yielded an identical (within stated errors) value of μ_0 like the present approach but a divergent value $g_0 = -4.2535(46)$. The latter result is a consequence of excluding u_1^{H} from fitted parameters; its presence precluded convergence of DS-cP because u_1^{H} strongly correlates[32] with t_0^{H}. In contrast, the present approach is insensitive to this effect and enables to evaluate both u_1^{H} and t_0^{H}, resulting in a reasonable estimation of g_0.

Applying the dissociation formula (eq 39) and values of GaH parameters c_i generated with Radiatom, we calculated $\mathcal{D}_e = -1.72 \times 10^8$ cm⁻¹ which differs significantly with experimental value $\mathcal{D}_e = 22906$ cm⁻¹. In order to avoid such inconsistency in the present work, we constrained

$$c_8 = \frac{\mathcal{D}_e}{2^{10}c_0} - \left(2^{-8} + \sum_{i=1}^{7} 2^{-8+i}c_i\right) \qquad \mathcal{D}_e = 22906 \text{ cm}^{-1} \tag{43}$$

to ensure physical significance of all potential parameters. The calculated value of $c_8 = -0.0581(47)$ is about 1/28 times the value $c_8 = -1.632(107)$ produced with Radiatom.[30]

In an analysis of the same GaH data Ogilvie and Liao[26] poorly determined adiabatic parameters $u_2^{Ga} = 5.515(830) \times 10^4$ cm⁻¹ and $u_3^{Ga} = 38.9(13.8) \times 10^4$ cm⁻¹. In a subsequent analysis[30]

these parameters were replaced with nonadiabatic vibrational ones $s_0^{Ga} = 0.539(81)$ and $s_1^{Ga} = 14.2(3.8)$, providing the same statistical characteristic of the fit as obtained previously. According to our results the presence in the fit of either u_i^{Ga} or s_i^{Ga} is questionable; for such a massive nuclide as gallium adiabatic and vibrational nonadiabatic effects are undetectable, possibly due in the latter case to a vibrational *immobility* of the heavy Ga center for which the BO approximation becomes satisfactory.

Our present approach appears to lack these disadvantages and produces radial parameters that form the most compact and physically meaningful representation of GaH data so far obtained.

We encountered similar circumstances for LiH data in the present work with circulating values of E_{vJ}. Table 2 reveals that this approach allows us to evaluate the nonadiabatic vibrational parameter $s_1^{H} = -2.00(16)$ indeterminate with both Radiatom and DS-cP; in the latter case its presence in the fit led to a divergent DS-c process, unlike in the present work in which reduction of 543 spectral data of LiH to $N = 13$ radial parameters is more efficient than that obtained with Radiatom ($N = 15$) and DS-cP ($N = 14$).

The proposed fitting procedure with circulating E_{vJ} is rapidly convergent and in the case of LiH requires three iterations (in comparison with 15 in DS-cP) to obtain parameters in a final set such that values alter less than their standard errors and affect insignificantly the precision of calculations. Initial values of fitted parameters were taken from Ogilvie's calculations.[30]

As in the present algorithm all mathematical formulae are derived in analytic form, one can apply this approach to quantitative analysis of spectral data using standard software for weighted nonlinear regression. To this goal vibrational term coefficients Y_{k0} can also be generated with Maple.[46,47] With such programs one can readily fit measured frequencies of numerous wavenumbers of transitions of multiple isotopic variants of a diatomic molecule to evaluate parameters of pertinent radial functions. The latter are an important source of information about the internal structure and physical properties including mechanical, extramechanical, and electromagnetic molecular properties.[30]

The results obtained in this work indicate that our extension of Dunham's approach can be expected to enable a contemporary spectroscopist to extend the range and depth of analysis of spectra measured at the present state of the art.

Appendix

To simplify calculations of the nth derivative b_n^{vJ} of the effective potential $U_{vJ}(\eta)$ with Maple, we rewrite eq 34 in the form

$$U_{vJ}(\eta) = \frac{B_{vJ}J(J+1)\left[1 + \sum_{i=0} c(i)z^i\right]}{(1+\eta)^2} + \sum_{i=0} d(i)z^i \tag{44}$$

in which

$$z = \frac{x_{vJ} + \eta(1 + x_{vJ})}{1 + [x_{vJ} + \eta(1 + x_{vJ})]/2} \quad (45)$$

$$c(i) = m_e \sum_{\mu=a,b} (t_i^\mu - s_i^\mu) m_\mu^{-1} \quad (46)$$

$$d(0) = E_{vJ} m_e \sum_{\mu=a,b} s_0^\mu m_\mu^{-1} \quad (47)$$

$$d(1) = m_e \sum_{\mu=a,b} (E_{vJ} s_1^\mu + u_1^\mu) m_\mu^{-1} \quad (48)$$

$$d(2) = m_e \sum_{\mu=a,b} (E_{vJ} s_2^\mu + u_2^\mu - c_0 s_0^\mu) m_\mu^{-1} + c_0 \quad (49)$$

$$d(i > 2) = m_e \sum_{\mu=a,b} [E_{vJ} s_i^\mu + u_i^\mu - c_0(s_{i-2}^\mu - \sum_{j=0}^{i-3} c_{i-2-j} s_j^\mu)] m_\mu^{-1} + c_0 c_{i-2} \quad (50)$$

Equation 44 ensures that the Maple output is in its most compact form, so that for example coefficient b_{12}^{vJ} (derivative of fourteenth order) written in Fortran optimized form, takes only 391 lines for $c(i)$ $i = 0...6$ and $d(i)$ $i = 0...15$.

The starting point to calculate x_{vJ} is the first derivative of the effective potential energy (eq 34)

$$f = \frac{dU_{vJ}(\eta)}{d\eta} = \frac{dU_{vJ}(x)}{d(x)} (1 + x_{vJ}) \quad (51)$$

in which

$$1 + x_{vJ} = \frac{dx}{d\eta} \qquad x = x_{vJ} + \eta(1 + x_{vJ}) \quad (52)$$

To calculate f, we rewrite eq 44 in the form

$$U_{vJ}(x) = \frac{B_0 J(J+1)[1 + \sum_{i=0} c(i) z^i]}{(1 + x)^2} + \sum_{i=0} d(i) z^i \quad (53)$$

in which

$$z = \frac{x}{1 + x/2} \quad (54)$$

Proceeding through eqs 28−32, one obtains x_{vJ} in an analytic form applied in calculations as a Maple output in optimized Fortran code. The Maple output is available from the author upon request.

References and Notes

(1) Dunham, J. L. *Phys. Rev.* **1932**, *41*, 713, 721.

(2) In this work, we use the notation B_0, R_0 instead of the standard one B_e, R_e, referring to quantities in the state with $J = 0$ and $v = 0$.

(3) Beckel, C. L.; Engelke, R. *J. Chem. Phys.* **1968**, *49*, 5199.

(4) Lemoine, B.; Demuynck, C.; Destombes, J. L.; Davies, P. B. *J. Chem. Phys.* **1988**, *89*, 673.

(5) Urban, R. D.; Magg, U.; Jones, H. *Chem. Phys. Lett.* **1989**, *154*, 135.

(6) Bahnmaier, A. H.; Urban, R. D.; Jones, H. *Chem. Phys. Lett.* **1989**, *155*, 269.

(7) Urban, R. D.; Bahnmaier, A. H.; Magg, U.; Jones, H. *Chem. Phys. Lett.* **1989**, *158*, 443.

(8) Urban, R. D.; Bahnmaier, A. H.; Birk, H.; Jones, H. *J. Chem. Phys.* **1990**, *92*, 14.

(9) Urban, R. D.; Birk, H.; Polomsky, P.; Jones, H. *J. Chem. Phys.* **1991**, *94*, 2523.

(10) Maki, A. G.; Olson, Wm. B.; Thompson, G. *J. Chem. Phys.* **1989**, *90*, 6887.

(11) Maki, A. G.; Olson, Wm. B.; Thompson, G. *J. Mol. Spectrosc.* **1990**, *144*, 257.

(12) Simons, G.; Parr, R. G.; Finlan, J. M. *J. Chem. Phys.* **1973**, *59*, 3229.

(13) Thakkar, A. J. *J. Chem. Phys.* **1975**, *62*, 1693.

(14) Mattera, L.; Salvo, C.; Terreni, S.; Thommasini, F. *J. Chem. Phys.* **1980**, *72*, 6815.

(15) Ogilvie, J. F. *Proc. R. Soc. Lond. A* **1981**, *378*, 287.

(16) Herman, R. M.; Asgharian, A. *J. Mol. Spectrosc.* **1966**, *19*, 305.

(17) Bunker, P. R. *J. Mol. Spectrosc.* **1970**, *35*, 306.

(18) Watson, J. K. G. *J. Mol. Spectrosc.* **1980**, *80*, 411.

(19) Herman, R. M.; Ogilvie, J. F. *Adv. Chem. Phys.* **1998**, *103*, 287.

(20) Fernández, F. M.; Ogilvie, J. F. *Chin. J. Phys.* **1992**, *30*, 177.

(21) Fernández, F. M.; Ogilvie, J. F. *Phys. Rev. A* **1990**, *42*, 4001.

(22) Nakagawa, K.; Uehara, H. *Chem. Phys. Lett.* **1990**, *168*, 96.

(23) Burenin, A. V.; Ryabikin, M. Yu. *J. Mol. Spectrosc.* **1989**, *136*, 140.

(24) Ogilvie, J. F. *J. Phys. B* **1994**, *27*, 47.

(25) Ogilvie, J. F.; Oddershede, J.; Sauer, S. P. A. *Chem. Phys. Lett.* **1994**, *228*, 183.

(26) Ogilvie, J. F.; Liao, S. C. *Chem. Phys. Lett.* **1994**, *226*, 281.

(27) Ogilvie, J. F. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3005.

(28) Ogilvie, J. F. *J. Mol. Spectrosc.* **1996**, *180*, 193.

(29) Ogilvie, J. F. *Mol. Phys.* **1996**, *88*, 1055.

(30) Ogilvie, J. F. *The Vibrational and Rotational Spectrometry of Diatomic Molecules*; Academic Press: London, 1998; Chapter 4.7.

(31) Molski, M. *Phys. Rev. A* **1994**, *50*, 4380.

(32) Molski, M. *J. Mol. Spectrosc.* **1997**, *181*, 1.

(33) Molski, M. *J. Mol. Spectrosc.* **1997**, *185*, 256.

(34) Molski, M. *J. Mol. Spectrosc.* **1999**, *193*, 244.

(35) Ogilvie, J. F.; Molski, M. *Spectrochim. Acta A* **1999**, 55.

(36) Molski, M. *Acta Phys. Pol., A*, submitted for publication.

(37) Campbell, J. M.; Dulick, M.; Klapstein, D.; White, J. B.; Bernath, P. F. *J. Chem. Phys.* **1993**, *99*, 8379.

(38) Ogilvie, J. F. *J. Chem. Phys.* **1988**, *88*, 2804.

(39) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold Co.: New York, 1979.

(40) Kim, G. B.; Balasubramanian, K. *J. Mol. Spectrosc.* **1989**, *134*, 412.

(41) Sauer, S. P. A. *Chem. Phys. Lett.* **1996**, *260*, 271.

(42) Petterson, L. G. M.; Langhoff, S. R. *J. Chem. Phys.* **1986**, *85*, 3130.

(43) Schwerdtfeger, P.; Heath, G. A.; Dolg, M.; Bennett, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 7518.

(44) Plummer, G. M.; Herbst, E.; de Lucia, F. C. *J. Chem. Phys.* **1984**, *81*, 4893.

(45) Yamada, C.; Hirota, E. *J. Chem. Phys.* **1988**, *88*, 6702.

(46) Ogilvie, J. F.; Monagan, M. B. *MapleTech* **1997**, *4*, 100.

(47) Fernández, F. M.; Ogilvie, J. F. *MapleTech* **1998**, *5*, 37.